Thermochromism of Polydiacetylene with a Hysteresis Loop in the Solid State and in Solution

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Partly crystalline polydiacetylene **1**, which is soluble in many organic solvents at room temperature, was prepared by the solid-state polymerization of 4-methoxybenzyl 10,12-pentacosadiynoate. We found a reversible change in the UV–vis absorption spectrum of **1** in a solid film, polymer matrix, and solution with a hysteresis loop as a function of temperature.

Conjugated polymers have attracted significant interest because they can be used for the fabrication of intelligent materials in various fields due to their intrinsic electronic, photonic, magnetic, and spectroscopic features.[1] Polydiacetylenes (PDAs) as one of the conjugated polymers are prepared by the solid-state polymerization of diacetylenes,[2] but they are often insoluble in solvents and have no melting point under their onset temperature of degradation. Therefore, they are used as a solid, thin film, or vesicle without further polymer processing after the in situ polymerization.[3–12] Such a poor solubility has resulted in limited applications, but it has been considered for a long time that strong intermolecular interactions, such as the hydrogen bond, are indispensable when forming a stacking structure for the solid-state polymerization, in which the diacetylene monomers are arranged in the appropriate stacking distance and angle.[3] At the same time, the strong intermolecular interaction simultaneously decreases the solubility of the resulting PDA.

Recently, we have synthesized a PDA soluble in common organic solvents without any strong intermolecular interaction and polar groups, on the basis of our results from the comprehensive investigation of the 1,3-diene polymerization in the crystalline state over the past decade.[13] The PDA **1** obtained from the solid-state polymerization of 4-methoxybenzyl 10,12-pentacosadiynoate (Chart 1) is highly crystalline and insoluble in organic solvents just after the polymerization, similar to other reported PDAs. However, **1** can be readily converted into partly crystalline and soluble polymer by reflux and reprecipitation. We have found that **1** shows a reversible thermochromism in the solid state and in solution. We now report a change in the UV–vis absorption spectra of **1** in the solid film, polymer matrix, and tetrahydrofuran (THF) as a function of temperature.

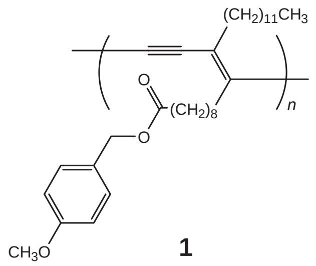

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Chart 1.

Polymer **1** was prepared by γ-radiation polymerization and was insoluble in the common organic solvents at room temperature due to its high crystallinity, but it was recovered as the partly crystalline polymer after reflux in 1,2-dichlorobenzene and reprecipitation. Polymer **1** with a lower crystallinity is soluble in organic solvents at room temperature and can be provided as a solution, which can be used for the fabrication of polymer films and blends by casting. Figure 1 shows a reversible change in the visible spectrum of **1** in the solid state. The red solid film of **1**, obtained by casting of the chloroform solution on a glass plate and then drying at room temperature, gave a visible absorption spectrum consisting of a broad peak around 490 nm and another sharp peak at 530 nm. The latter is due to the J aggregates.[14] During a heating process to 130 °C, the broad peak shifted to a lower wavelength region (blue shift) and the intensity of the peak observed at 530 nm decreased without any shift in the wavelength. A single broad peak was observed at 445 nm and the polymer film was yellow at 130 °C. This color change was reversible below 130 °C, but further heating resulted in an irreversible color change. After heating to 150 °C, the wavelength of the broad peak was lower than that before heating by 20 nm. The spectral change observed in this study is accounted for by a change in the polymer conformation depending on the crystallization of the side chain. In fact, in the DSC trace of **1** upon heating, the melting of the side chain of **1** was observed at 127.7 °C. The crystallization of the long alkyl chains in the side groups of **1** was also confirmed by IR spectroscopy under temperature control. An absorption due to the methylene groups observed at 2850 and 2917 cm^{-1} at room temperature gradually shifted

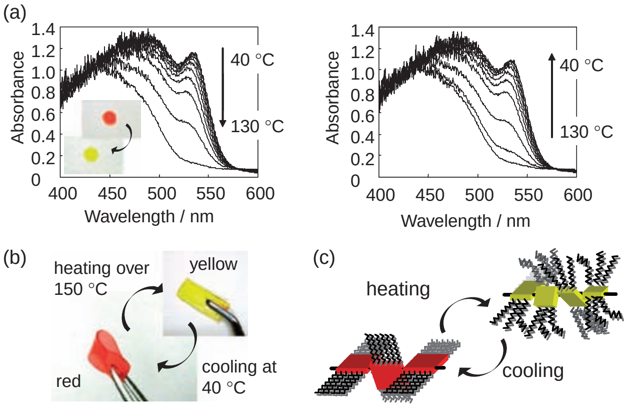

Figure 1. (a) Reversible change in the visible spectrum of **1** in the solid state. The insert indicates the appearance of **1** at 40 (red) and 130 °C (yellow). (b) Change in the color of **1** embedded in poly(vinyl alcohol) matrix. (c) Schematic model for side chain crystallization and a change in the polymer conjugating length.

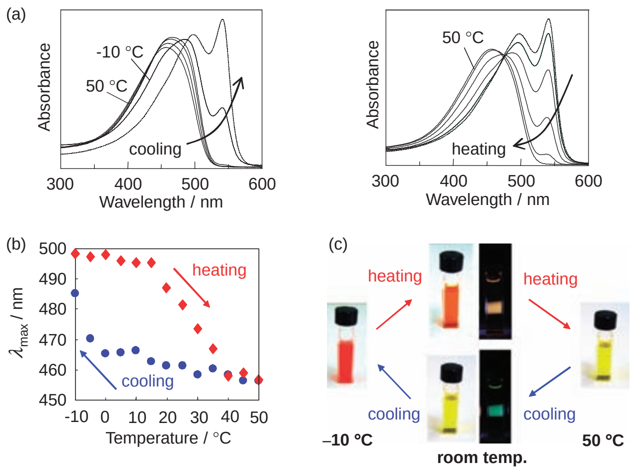

Figure 2. (a) Reversible change in the absorption spectrum of **1** in THF during cooling and heating processes in the range of 50 to −10 °C. The dotted curve was measured at −10 °C after the solution was once cooled to −78 °C. (b) Change in the λ_{max} value during heating and cooling processes. (c) Color change in the THF solution of **1**. Right figures at room temperature are the emission of orange and green lights from the red and yellow solutions, respectively. Excitation wavelength is 365 nm.

to a higher wavenumber region and reached constant values as 2855 and 2926 cm^{-1}, respectively. This is due to a change in the conformation of the alkyl chains from a trans zigzag structure packed in the crystalline state at room temperature to a disturbed one at a higher temperature. The reversible color change was observed not only for the solid film, but also in a polymer matrix using poly(vinyl alcohol) (Figure 1b) or poly(methyl methacrylate). A domain of **1** in the polymer matrix by phase separation was detected by transmission electron microscopy.

Interestingly, a similar thermochromism of **1** was also observed in solution. Figure 2 shows a change in the UV–vis spectrum of the THF solution of **1**. The spectrum was completely reversible, and a clear hysteresis loop was observed. The peak at 498 nm retained its wavelength when it was heated from −10 to 15 °C, and then shifted to a lower wavelength region. A single peak was observed at 50 °C (λ_{max} = 457 nm). During the cooling process, the peak top gradually shifted to the longer wavelength region in the temperature range between 50 and 10 °C, and then a large shift was observed below 10 °C. Consequently, we can obtain different color solutions at room temperature due to the hysteresis of the absorption property of **1**, as shown in Figure 2c. The red and yellow solutions showed the emission of orange and green visible lights, as expected. The red solution provided a stronger emission, while no emission was observed from **1** in the solid state.

In the present study, we have determined the reversible thermochromism of PDA in not only the solid state, such as solid films and a polymer matrix, but also in solution. The preliminary light scattering and NMR measurements of the THF solution of **1** suggested the formation of polymer aggregates at a low temperature. The aggregation and rearrangement of the polymer chains may play an important role for the thermochromism in solution. The characterization and mechanism for the aggregation of polymer chains in solution as well as the effect of the side chain structure of PDA are now under investigation.

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